Available online at www.sciencedirect.com
SCIENCE DIRECT®
Mendeleev Commun., 2007, **17**, 274–276
Mendeleev Communications

High selectivity of fluorine atom addition to the asymmetric chemical bonds of C_{70} fullerene

Eugenii Ya. Misochko,*[a] Alexander V. Akimov,[a] Vasilii A. Belov,[a] Daniil A. Tyurin[b] and Dmitry N. Laikov[c]

[a] *Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 496 515 5420; e-mail: misochko@icp.ac.ru*
[b] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119992 Moscow, Russian Federation*
[c] *Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122, USA*

DOI: 10.1016/j.mencom.2007.09.008

New assignment of EPR spectra of low-temperature F + C_{70} reaction products shows an unexpectedly high selectivity of the addition of the F atom to the asymmetric C=C bonds of C_{70} to form three $C_{70}F$ regioisomers only among the five possible ones.

Synthesis of new compounds, such as the fullerene derivatives $C_{60}R_n$ and $C_{70}R_n$ (n = 2, 4, 6, …), involves a radical cascade process, which implies the formation of a radical intermediate on each odd stage (n = 1, 3, 5, …). Thus, the radical reactions play a key role in the formation of various regioisomers in the final products.[1] The fullerene C_{70} has an ellipsoidal shape, so that the radical addition to it can give rise to five isomeric $C_{70}R$ adducts **A**, **B**, **C**, **D** and **E**, named after the five distinct carbon atoms of C_{70} to which the radical can add (see Figure 1). The radical adduct is formed upon addition of reactive atom (or radical) to one of the unsaturated double bonds, $C_{\mathbf{A}}$=$C_{\mathbf{B}}$, $C_{\mathbf{C}}$=$C_{\mathbf{C}}$, and to the carbon bonds on the equatorial hexagons, $C_{\mathbf{D}}$=$C_{\mathbf{D}}$ and $C_{\mathbf{D}}$=$C_{\mathbf{E}}$. Previous EPR measurements have shown that the three isomeric $C_{70}R$ monoadducts are formed in most cases if the reaction occurs in solution at ambient temperatures. However, a definite assignment of the observed spectra to the specific regioisomers based on the measured isotropic hyperfine constants (hfc's) is hampered because of their relatively small differences. Morton *et al.*[2] proposed that the observed spectra of F + C_{70} reaction products should correspond to the regioisomers **A**, **B** and **C**. On the contrary, a conclusion was made[3,4] that isomer **D** should be the most abundant in the EPR spectra of a series of alkyl, aryl and fluoroalkyl radicals $C_{70}R$. In this work we have measured, for the first time, the anisotropic spectrum of $C_{70}F$ regioisomers generated in a solid argon matrix. Based on the observed spectra, both isotropic [$A_{iso} = (A_{\parallel} + 2A_{\perp})/3$] and magnetic-dipole interaction [$A_{dip} = (A_{\parallel} - A_{\perp})/3$] hfc's of the axially symmetric hf interaction tensor on ^{19}F nucleus have been determined. Comparison of the measured hfc's with the theoretical values from a careful quantum-chemical calculation leads to a new assignment of the spectra to the generated isomers, which strongly differs from the previous ones. Our new assignment allowed us to make the conclusion that the addition of F atom to the asymmetric C=C bonds of C_{70}, namely $C_{\mathbf{A}}$=$C_{\mathbf{B}}$ and $C_{\mathbf{D}}$=$C_{\mathbf{E}}$, shows a high selectivity producing only one of the isomers, **A** and **D**, respectively.

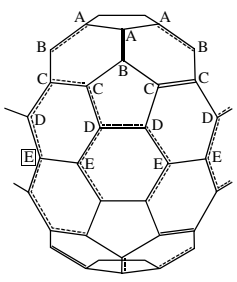

Figure 1 Picture of the five different carbon groups on the C_{70} ellipsoid.

Previously,[5] we have developed a new cryogenic methodology for the generation and EPR studies of the radicals $C_{60}F$ in a solid argon matrix. A similar experimental technique was used in this study. Solid argon films were prepared by vacuum co-deposition of two separate molecular beams (Ar/F_2 and C_{70} vapour) onto a substrate cooled to 15 K. The mole fraction of reactants (F_2 and C_{70}) was less than 10^{-3}. The dissociation of F_2 was performed by 337 nm laser photolysis. Photodissociation of F_2 yields two translationally excited F atoms with ~1 eV excess kinetic energy per atom. The fluorine atoms undergo thermally activated diffusion in the solid argon at temperatures above 20 K.[6] To distinguish the chemical reactions involving the photogenerated 'hot' F atoms and the diffusing thermal F atoms, photolysis was performed at 15 K, after which the photolysed samples were annealed at T > 20 K to initiate the reactions of diffusing F atoms.

The photolysis of F_2 at 15 K gives rise to the EPR spectrum of stabilised radicals. Intensities of EPR lines increase proportionally to the photolysis time at the initial stage and reach limiting values under extensive photolysis. The obtained spectrum

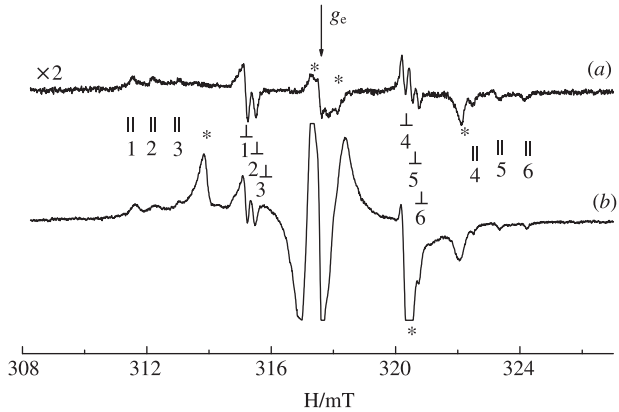

Figure 2 EPR spectra of the sample $Ar/C_{70}/F_2$ at 15 K: (*a*) after UV photolysis of F_2 at 15 K; (*b*) subsequent annealing of the photolysed sample at 26 K. Lines of FO_2 radicals are marked with asterisks (see the text). Six parallel and perpendicular components are marked with (∥) and (⊥), respectively.

Table 1 Hyperfine constants on ^{19}F for the regioisomers $C_{70}F$.

Radical species	A_{iso}/mT (in liquid solution)[a]	In solid argon (this work)[b]			
		A_{iso}/mT	A_{dip}/mT	Assignment of the EPR lines[c]	Assignment of the regioisomers
I	7.44 w (**A**)	7.54, 7.56, 7.54 (7.55)	2.24, 2.23, 2.24 (2.24)	‖: 2-6, 2-6, 2-6 ⊥: 3-6, 2-5, 3-6	**C**
II	7.41 m (**B**)	7.49, 7.48, 7.52 (7.50)	2.16, 2.17, 2.15 (2.16)	‖: 1-5, 1-5, 1-5 ⊥: 2-5, 3-6, 1-5	**A**
III	6.52 vs (**C**)	6.57, 6.57, 6.54 (6.56)	1.55, 1.55, 1.56 (1.55)	‖: 3-4, 3-4, 3-4 ⊥: 1-4, 1-4, 2-4	**D**
IV[d]	5.35 w (**D**)				

[a]Solvent, *tert*-butylbenzene at 325 K; data from ref. 2; an assignment of the regioisomers $C_{70}F$ performed in ref. 2 is given in parentheses. [b]Three sets of hf parameters are given (see the text). The average values of hfc's are given in parentheses. [c]Numbering of the EPR lines corresponding to the parallel (‖) and perpendicular (⊥) patterns in the spectrum is shown in Figure 2. [d]Solvent, toluene at 325 K; data from ref. 2.

[Figure 2(*a*)], corresponds to a superposition of spectra of different radicals. Broad anisotropic doublet centered in the region of free electron *g*-factor corresponds to the radical $FO_2^{\cdot}$ formed by the addition of F atoms to O_2 molecules. Molecular oxygen is a common impurity in commercial fluorine gas; therefore, the $FO_2^{\cdot}$ radicals are always present in the samples under our experimental conditions.[5,6] The other series of anisotropic EPR lines consist of three pairs of parallel and perpendicular components. It corresponds to three randomly oriented radical species with doublet hyperfine splitting. Annealing of the photolysed samples to 26 K leads to a prevalent growth of the $FO_2^{\cdot}$ radicals [Figure 2(*b*)]. The intensity of the other spectra increases two to four times. The doublet hyperfine structure appears in the spectrum due to the interaction of the unpaired electron with ^{19}F ($I = 1/2$) nucleus. Therefore, six pairs of hf components in the observed new spectrum can be assigned to the three regioisomers of $C_{70}F$. A simple assignment of the spectrum seems impractical because all of the hf components have very close intensities and magnetic parameters. Nevertheless, the possible limiting values of the isotropic hfc's for the generated radicals could be determined from the spectra shown in Figure 2. The highest splitting in the anisotropic components corresponds to the possible highest value of $A_{iso}(max) = 7.92$ mT, and the lowest splitting corresponds to the lowest value of $A_{iso}(min) = 6.25$ mT. Morton *et al.*[2] have obtained four doublet splittings in the spectrum of the $F + C_{70}$ reaction products in liquid solution (Table 1). As it can be seen, the A_{iso} hfc's of radicals (**I**–**III**) in the liquid lie inside the interval 7.92–6.25 mT, as determined for A_{iso} of the three radicals in solid argon.

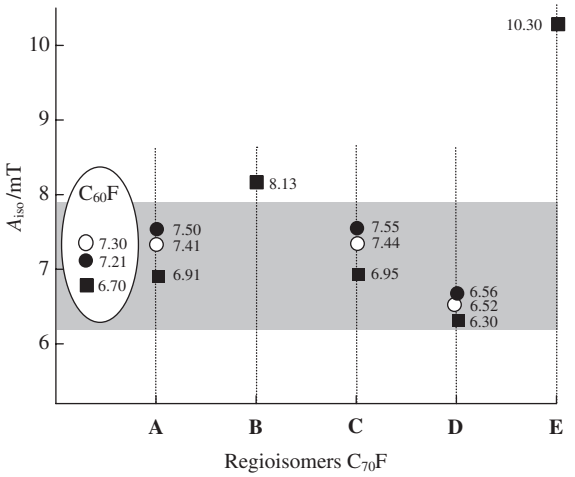

Figure 3 Calculated isotropic hf constants for the five regioisomers of $C_{70}F$ (DFT method: PBE1/Λ22m, optimised geometry), dark squares. The three hfc's obtained in liquid solution in ref. 2 are shown with open circles; the three hfc's obtained in solid argon are shown with solid circles. Data for the radical $C_{60}F$ from refs. 5 and 2 are shown in the oval inset. Gray area shows the limiting interval (7.92–6.25 mT) for isotropic hfc's in solid argon, see the text.

We have shown[5] that density-functional calculations using a hybrid PBE functional and highly optimised basis sets give the theoretical values of hfc's in good agreement with the experimental measurements for the radical $C_{60}F$ (Table 2). Here we have performed such calculations for the regioisomers of $C_{70}F$ to make a definite assignment of the observed species. The results of the calculations are shown in Table 2 and Figure 3. Comparison between the calculated and experimentally measured isotropic hfc's definitely shows that the three regioisomers, **A**, **C** and **D**, have the calculated A_{iso} very close to those observed in liquid solution for species **I**–**III**. The parameters A_{iso} for these species lie inside the interval for A_{iso} of the three radicals in solid argon. At the same time, the calculated parameters A_{iso} for the regioisomers **B** and **E** exceed the value $A_{iso}(max)$ in solid argon. Based on these facts we have concluded that the $F + C_{70}$ reactions in liquid solution and in solid argon generate the same radical species **I**, **II** and **III**, which correspond to regioisomers **C**, **A** and **D** only. Regioisomers **B** and **E** are not generated in the studied system.

To carry out an assignment of the observed spectrum, we have selected the combinations of hyperfine patterns satisfying the following requirements: (*a*) all of the three hfc's A_{iso} should agree with those for radicals **I**, **II** and **III** with an accuracy of ±0.1 mT; (*b*) three pairs of the corresponding parameters A_{iso} and A_{dip} should comply with the calculated parameters for the isomers **A**, **C** and **D**. The best three sets of hf parameters selected are shown in Table 1 and Figure 3. The obtained hf parameters in these three combinations have very close values mainly because of very small differences in the resonance magnetic fields for the perpendicular components 1 and 2, as shown in Figure 2.

As evident from Table 1, the performed assignment differs drastically from the previous one.[2] Tables 1 and 2 show that radical **IV** obtained in liquid (which has very weak intensities of EPR lines) cannot be assigned to the regioisomers of $C_{70}F$. Our reassignment of the spectra of $C_{70}F$ regioisomers gives evidence that the reason for the generation of only three regioisomers in the reaction $F + C_{70}$ consists in the high selectivity of the product formation if reactive atom attacks asymmetric

Table 2 Calculated hyperfine parameters on ^{19}F for the regioisomers $C_{70}F$ (PBE1/Λ22m//PBE1/Λ22m).

Radical	Hyperfine constants/mT	
	A_{iso}	A_{dip}
$C_{70}F$(**A**)	6.91	2.18
$C_{70}F$(**B**)	8.13	2.53
$C_{70}F$(**C**)	6.95	2.35
$C_{70}F$(**D**)	6.29	1.85
$C_{70}F$(**E**)	10.29	3.27
$C_{60}F$[a]	6.70	2.16

[a]Data from ref. 5, experimental data for $C_{60}F$ in solid argon: $A_{iso} = 7.21$ mT and $A_{dip} = 1.85$ mT.

C=C bonds, such as C_A=C_B and C_D=C_E. Only the isomer $C_{70}F$(**A**) is formed if the F atom adds to the C_A=C_B bond, and only the isomer $C_{70}F$(**D**) is formed if the F atom adds to the C=C bond on the equatorial hexagons. The third isomer, $C_{70}F$(**C**), is formed if the F atom adds to the symmetric C_C=C_C bond.

This work was supported by the Russian Foundation for Basic Research (grant no. 04-03-32599) and the Russian Academy of Sciences (programme no. OKh-01).

References

1 (*a*) B. L. Tumanskii and O. G. Kalina, in *Radical Reactions of Fullerenes and their Derivatives*, Kluwer Academic Publishers, Dordrecht, 2002; (*b*) L. N. Sidorov and O. V. Boltanina, *Usp. Khim*., 2002, **71**, 611 (*Russ. Chem. Rev.*, 2002, **71**, 535); (*c*) K. Thilgen and F. Diederich, *Chem. Rev.*, 2006, **106**, 5049.

2 J. R. Morton, K. F. Preston and F. Negri, *Chem. Phys. Lett*., 1994, **221**, 59.

3 R. Borghi, L. Lunazzi, G. Placucci, P. J. Krusic, D. A. Dixon, N. Matsuzawa and M. Ata, *J. Am. Chem. Soc*., 1996, **118**, 7608.

4 R. Borghi, L. Lunazzi, B. Guidi and G. Placucci, *J. Org. Chem*., 1996, **61**, 5667.

5 E. Ya. Misochko, A. V. Akimov, V. A. Belov and D. A. Tyurin, *Izv. Akad. Nauk, Ser. Khim*., 2007, 424 (*Russ. Chem. Bull., Int. Ed.*, 2007, **56**, 438).

6 E. Ya. Misochko, A. V. Akimov, I. U. Goldshleger, D. A. Tyurin and D. N. Laykov, *J. Chem. Phys*., 2005, **125**, 4503.

Received: 26th March 2007; Com. 07/2896